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(54) LEAD-FREE ELECTROLESS TIN ALLOY PLATING BATH AND PLATING METHOD,
AND ELECTRONIC PARTS HAVING LEAD-FREE TIN ALLOY FILM FORMED BY USING
THE ELECTROLESS PLATING BATH

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a plating bath excellent in the joining strength and corrosion resistance of a film to be obtained and increased in the velocity of precipitation by making it possible to regulate a bath so as to form a lead-free tin alloy film which contains a mixture of stannous salt and salts of one or more kinds among eight metals such as Bi, one or more kinds among organic acids and inorganic acids, and a complexing agent and in which the composition ratio of the above metals forming an alloy together with tin is regulated to a specific value or above.

SOLUTION: The plating bath contains the following (A), (B), (C): (A) a soluble metallic salt mixture of stannous salt and a salt of at least one metal selected from the group consisting of Bi, In, Sb, Zn, Co, Ag, and Cu; (B) at least one acid selected from organic acids, such as organic sulfonic acid and carboxylic acid, and inorganic acids, such as hydrochloric acid, sulfuric acid, and borofluoric acid; (C) a complexing agent. Further, the composition ratio of the above metals, such as Bi, forming an alloy together with tin is regulated to ≥ 3 wt.% in total. The velocity of precipitation and the quality of a plating film are improved by further adding a reducing agent and a surface active agent.

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CLAIMS

[Claim(s)]

[Claim 1] (A) ** stannous salt, ** bismuth and an indium, antimony, zinc, Cobalt, nickel, silver, the mixture of a fusibility metal salt with the salt of at least a kind of metal chosen from the group which consists of copper, (B) Organic acids, such as an organic sulfonic acid and a carboxylic acid, or a hydrochloric acid, a sulfuric acid, So that at least a kind of acid chosen from inorganic acids, such as fluoroboric acid, and the (C) complexing agent may be contained, it may change and the tin alloy coat in which the presentation ratio of the metal of (A)-** which generates tin and an alloy does not contain 3% of the weight or more of lead in a total amount may be formed The non-electrolyzed tin alloy plating bath of the lead free-lancer characterized by enabling adjustment of a bath.

[Claim 2] That whose non-electrolyzed tin alloy plating bath according to claim 1 is a lead free-lancer's permutation mold radio solution tin alloy plating bath.

[Claim 3] The non-electrolyzed tin alloy plating bath of the lead free-lancer characterized by adding a reducing agent to an electroless deposition bath according to claim 1 or 2 further.

[Claim 4] The non-electrolyzed tin alloy plating bath of the lead free-lancer characterized by adding a surfactant further at an electroless deposition bath given in any 1 term of claims 1-3.

[Claim 5] Electronic parts in which the tin alloy coat which is immersed in a non-electrolyzed tin alloy plating bath given in any 1 term of claims 1-4 in electronic parts, and does not contain lead was formed.

[Claim 6] That whose electronic parts according to claim 5 are the tape carrier packages of TAB.

[Claim 7] (A) ** stannous salt, ** bismuth and an indium, antimony, zinc, Cobalt, nickel, silver, the mixture of a fusibility metal salt with the salt of at least a kind of metal chosen from the group which consists of copper, (B) The non-electrolyzed tin alloy plating bath which contains at least a kind of acid chosen from inorganic acids, such as organic acids, such as an organic sulfonic acid and a carboxylic acid, or a hydrochloric acid, a sulfuric acid, and fluoroboric acid, and the (C) complexing agent is used. A lead free-lancer's non-electrolyzed tin alloy plating approach that the presentation ratio of the metal of (A)-** which generates tin and an alloy is characterized by forming the tin alloy coat which is 3 % of the weight or more and which does not contain lead in a total amount.

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JP,11-021673,A-[DETAILED DESCRIPTION]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] Since this invention does not contain lead about the tape carrier package for TAB in which the non-electrolyzed tin alloy coat was formed etc., by the plating bath concerned in the non-electrolyzed tin alloy plating bath (lead free-lancer) which does not contain lead and the plating approach, and a list, even if the bad influence to the body or an environment compares it with a non-electrolyzed tin coat few tops, it offers what can form the high tin alloy coat which is whenever [equal practical-use] with a deposit rate, bonding strength, and corrosion resistance.

[0002]

[Description of the Prior Art] Generally, tinning on copper and a copper alloy is widely used for electronic parts, the package for semiconductor devices (especially TAB method), etc. from the reason nil why good bonding nature is securable with the outstanding soldering nature etc. However, a whisker occurs, a tinning coat tends to cause a short circuit, and it divides, and in the high-density-assembly article to which a miniaturization, complication, and many pin-ization are progressing quickly, this evil will be serious and will reduce dependability, such as TAB, remarkably.

[0003] Then, although performing annealing treatment to a tinning coat and preventing generating of a whisker is performed, the counter diffusion between the copper and tin which constitute a lead by annealing treatment advances, a tin metal layer becomes thin, bonding nature is spoiled or a possibility that productivity may fall comes out.

[0004]

[Problem(s) to be Solved by the Invention] Then, it is possible as other approaches of solving the problem of the above-mentioned whisker to change for example, a plating coat to a tin-lead alloy from tin. This tin-lead alloy plating coat has the low melting point, and it excels also in soldering nature, but on the other hand we are anxious about the leaden effect of toxic to health or an environment, and, recently, the motion which is going to regulate the tin alloy containing lead itself has also come out. On the other hand, in the electronic parts of said TAB method, and the fine pitch printed-circuit board of SMT correspondence, the demand to accelerating-izing of the deposit rate of an electroless deposition bath, bonding strength of the plating coat obtained, corrosion resistance improvement from the standpoint of the endurance of improvement in workability, a cost cut, or a coat, etc. is severe every year.

[0005] In the electroless deposition bath of a tin alloy without the problem of a tin whisker, this invention is excellent in the bonding strength of a tin alloy coat and corrosion resistance which are acquired, and makes it a technical problem to develop the plating bath of a lead free-lancer with a quick deposit rate.

[0006]

[Means for Solving the Problem] It was JP,8-296050,A, these people used the electroless deposition bath containing the fusibility salt of the first tin, and the fusibility salt of the specific metal chosen from a bismuth, an indium, lead, and antimony, formed the plating coat so that the thickness of a deposit coat

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might be 0.1-1.0 micrometers, and indicated the approach of preventing the tin whisker of a plating coat effectively while the presentation ratio of the above-mentioned specific metal in a deposit coat was 0.1 - 3.0 % of the weight in the total amount. It is characterized by obtaining the plating coat of the outstanding bonding strength while it prevents a tin whisker effectively, even if the well-known technique concerned omits annealing treatment by extracting to the thin range of specification [the thickness of a plating coat], and limiting the content of a specific metal to the predetermined minute amount range.

[0007] this invention persons studied wholeheartedly whether moreover the thought of this well-known technique of limiting the presentation ratio of the specific metal in a plating coat to a minute amount would be reversed, the non-electrolyzed tin alloy plating bath which increased the presentation ratio of the specific metal in a coat would be chosen as the candidate for research, and sufficient practicality for bonding strength, a deposit rate, etc. of a tin alloy coat which were obtained could be given, making the above-mentioned well-known technique into a starting point. consequently, a specific metal -- lead -- even when free, even if it measured the bonding strength of the tin alloy plating coat obtained as the presentation ratio in that coat is more than predetermined even if it extends the class of this specific metal from the above-mentioned well-known technique in addition -- and, corrosion resistance, and a deposit rate against the non-electrolyzed tin coat, they traced it being equal or excelling, and completed this invention.

[0008] This invention 1 Namely, (A) ** stannous salt, and ** bismuth, an indium, Antimony, zinc, cobalt, nickel, silver, the mixture of a fusibility metal salt with the salt of at least a kind of metal chosen from the group which consists of copper, (B) Organic acids, such as an organic sulfonic acid and a carboxylic acid, or a hydrochloric acid, a sulfuric acid, So that at least a kind of acid chosen from inorganic acids, such as fluoroboric acid, and the (C) complexing agent may be contained, it may change and the tin alloy coat in which the presentation ratio of the metal of (A)-** which generates tin and an alloy does not contain 3% of the weight or more of lead in a total amount may be formed It is the non-electrolyzed tin alloy plating bath of the lead free-lancer characterized by enabling adjustment of a bath.

[0009] This invention 2 is characterized by the non-electrolyzed tin alloy plating bath of above-mentioned this invention 1 being a lead free-lancer's permutation mold radio solution tin alloy plating bath.

[0010] This invention 3 is the non-electrolyzed tin alloy plating bath of the lead free-lancer characterized by adding a reducing agent to above-mentioned this invention 1 or the electroless deposition bath of 2 further.

[0011] This invention 4 is the non-electrolyzed tin alloy plating bath of the lead free-lancer characterized by adding a surfactant to one electroless deposition bath of above-mentioned this inventions 1-3 further.

[0012] This invention 5 is the electronic parts in which the tin alloy coat which is immersed in one non-electrolyzed tin alloy plating bath of above-mentioned this inventions 1-4 in electronic parts, and does not contain lead was formed.

[0013] This invention 6 is characterized by the electronic parts of above-mentioned this invention 5 being the tape carrier packages of TAB.

[0014] This invention 7 (A) ** stannous salt, ** bismuth and an indium, antimony, Zinc, cobalt, nickel, silver, the mixture of a fusibility metal salt with the salt of at least a kind of metal chosen from the group which consists of copper, (B) The non-electrolyzed tin alloy plating bath which contains at least a kind of acid chosen from inorganic acids, such as organic acids, such as an organic sulfonic acid and a carboxylic acid, or a hydrochloric acid, a sulfuric acid, and fluoroboric acid, and the (C) complexing agent is used. The presentation ratio of the metal of (A)-** which generates tin and an alloy is the non-electrolyzed tin alloy plating approach of the lead free-lancer characterized by forming the tin alloy coat which is 3 % of the weight or more, and which does not contain lead in a total amount.

[0015]

[Embodiment of the Invention] The presentation ratio of the specific metal which this invention 1 considers divalent tin<4> salt, tin and the salt of the specific metal which generates an alloy, an acid,

and a complexing agent as a basic presentation, and generates the tin of the tin alloy coats obtained and an alloy is the non-electrolyzed tin alloy plating bath of the lead free-lancer characterized by being 3 % of the weight or more, this invention 3 carries out a reducing agent at this bath, and this invention 4 carries out additional mixing of the surfactant respectively.

[0016] Moreover, the non-electrolyzed tin alloy plating bath of the lead free-lancer of this invention 1 means the non-electrolytic bath of a superordinate concept including both a permutation mold radio solution tin alloy plating bath and an autocatalysis mold radio solution tin alloy plating bath. The above-mentioned permutation mold radio solution tin alloy plating bath is shown in this invention 2, and says the non-electrolytic bath of the type with which the parent metal (it is the after-mentioned like for example, copper or a copper alloy) which is the plated field where a tin alloy coat deposits serves as a metal ion by the chemical replacement reaction in an electroless deposition process, and is eluted during a bath. On the other hand, an autocatalysis mold radio solution tin alloy plating bath means the non-electrolytic bath with which the parent metal which is the plated field of a tin alloy serves as a metal ion in an electroless deposition process, and says the non-electrolytic bath of the type which is not eluted during a bath, or gives catalysts, such as palladium, to the plated field of nonmetals, such as plastics and ceramics, and deposits a tin (carrying out nucleus attachment) alloy. In this case, since the metal (namely, parent metal) plated or the palladium itself given to the nonmetal side only serves as a catalyst of a reduction plating reaction, an autocatalysis mold is called. For example, although the non-electrolyzed tin-lead alloy bath to which the non-electrolytic copper plating bath which uses formaldehyde as a reducing agent, the electroless-nickel-plating bath which uses hypophosphite as a reducing agent belong to this autocatalysis mold electroless deposition bath, and uses a titanium trichloride as a reducing agent as a tin alloy bath of an autocatalysis mold is known, it is possible to apply this autocatalysis method to a lead free-lancer's non-electrolyzed tin alloy bath in this invention.

[0017] The above-mentioned specific metals which generate tin and an alloy are a bismuth, an indium, antimony, zinc, cobalt, nickel, silver, and copper. As an example of a tin alloy The tin alloy of 3 component systems, such as tin-nickel-zinc and tin-copper-zinc, is also contained at first in the tin alloy of the two-component system of a tin-bismuth, a tin-indium, tin-antimony, tin-zinc, tin-cobalt, tin-nickel, tin-silver, and tin-copper.

[0018] As the above-mentioned stannous salt, although the salts of the fusibility of arbitration can be used; salts with the below-mentioned acid (especially organic sulfonic acid) are desirable, and can also use the complex salt (water solubility) obtained by dissolving a metal or a metallic oxide in the acid concerned. Although the salt of said specific metal which generates tin and an alloy, on the other hand, means the fusibility salt of the arbitration which generates various kinds of metal ions (Bi^{3+} , In^{3+} , Sb^{3+} , Zn^{2+} , Co^{2+} , Co^{3+} , nickel^{2+} , Ag^{+} , Cu^{+} , Cu^{2+} , etc.) under a plating bath and the example is as follows Especially, salts with the below-mentioned acid (especially organic sulfonic acid) are desirable.

[0019] (1) Oxide : Bi_2O_3 , In_2O_3 , ZnO , Ag_2O , Cu_2O , CuO , CoO , NiO , etc.

(2) Halogenide : BiCl_3 , InCl_3 , BiI_3 , InI_3 , ZnCl_2 , ZnBr_2 , ZnI_2 , BiBr_3 , InBr_3 , AgCl , AgBr , CuCl , CuBr , CuI , SbCl_3 , CoCl_2 , NiCl_2 , etc.

(3) A salt with an inorganic acid and an organic acid, other : bismuth nitrates, a sulfuric-acid bismuth, Indium sulfate, a zinc sulfate, a methansulfonic acid indium, an ethane-sulfonic-acid indium, A methansulfonic acid bismuth, a 2-propanol sulfonic-acid bismuth, A p-phenolsulfonic acid bismuth, methansulfonic acid zinc, p-phenolsulfonic acid zinc, Tartaric-acid antimony, a silver nitrate, methansulfonic acid silver, citric-acid silver, the second copper of p-phenolsulfonic acid, Cu_3P , CuSCN , $\text{CuBr}(\text{S}(\text{CH}_3)_2)$, methansulfonic acid antimony, hoe antimony fluoride, cobalt sulfate, cobaltous acetate, a nickel sulfate, methansulfonic acid nickel, etc.

[0020] the fusibility salt of the above-mentioned specific metal -- single -- business -- or it can use together. Although this invention does not obtain the tin alloy coat from which the presentation ratio of a specific metal becomes 3% of the weight or more by enabling adjustment of the addition of the fusibility salt of the tin to an electroless deposition bath, and the fusibility salt of this specific metal and especially the total concentration (conversion addition as a metal) of tin and a specific metal is not asked, generally it can be made 1 - 100 g/L extent. There is not necessarily no presentation ratio of the specific metal in

the tin alloy coat obtained from the content and the plating bath under electroless deposition bath of a specific metal ion in the most important proportionality. In this case, so to speak Although it is in a loose correlation in many cases, if this contractor has Based on a rule of thumb, the presentation ratio of the specific metal in a tin alloy coat can be adjusted more than amount [of Sadashige Tokoro] % by changing a class, content, etc. of plating bath temperature, the churning degree of a plating bath, plating time amount or a complexing agent, a reducing agent, a surfactant, etc.

[0021] However, both the presentation ratios in the deposit coat of the above-mentioned specific metal have a standpoint to 3 - 70 desirable % of the weight which holds the bonding strength of a plating coat, corrosion resistance, and **** capacity on practical use level. Moreover, it is desirable to control bonding strength and corrosion resistance from the standpoint raised good to 3 - 30% of the weight.

[0022] Although organic acids, such as organic sulfonic acids, such as an alkane sulfonic acid with the comparatively moderate reaction in a plating bath, an alkanol sulfonic acid, and an aromatic series sulfonic acid, or a carboxylic acid, are desirable as the above-mentioned acid, inorganic acids, such as a hydrochloric acid, fluoroboric acid, a sulfuric acid, a silicofluoric acid, and perchloric acid, can also be chosen. the above-mentioned acid - single - business - or it is used together and, generally the addition of an acid is 10 - 150 g/L preferably 0.1 to 200 g/L.

[0023] As the above-mentioned alkane sulfonic acid, what is shown by chemical formula $C_nH_{2n+1}SO_3H$ (for example, $n=1-5$, preferably 1-3) can be used, and, specifically, a hexane sulfonic acid, the Deccan sulfonic acid, a dodecane sulfonic acid, etc. are mentioned outside methansulfonic acid, ethane sulfonic acid, 1-propane sulfonic acid, 2-propane sulfonic acid, 1-butane sulfonic acid, 2-butane sulfonic acid, a pentane sulfonic acid, etc.

[0024] As the above-mentioned alkanol sulfonic acid, chemical formula $C_mH_{2m+1}-CH(OH)-C_pH_2-p-SO_3H$ What is shown by ($m=0-2$, $p=1-3$) can be used. Specifically [for example,] A 2-hydroxy ethane-1-sulfonic acid, a 2-hydroxy propane-1-sulfonic acid, Besides [of a 2-hydroxy butane-1-sulfonic acid, a 2-hydroxy pentane-1-sulfonic acid, etc.], A 1-hydroxy propane-2-sulfonic acid, a 3-hydroxy propane-1-sulfonic acid, A 4-hydroxy butane-1-sulfonic acid, a 2-hydroxy hexane-1-sulfonic acid, a 2-hydroxy decane-1-sulfonic acid, a 2-hydroxy dodecane-1-sulfonic acid, etc. are mentioned.

[0025] The above-mentioned aromatic series sulfonic acids are benzenesulfonic acid and a naphthalene sulfonic acid (for example, 2-naphthalene sulfonic acid) fundamentally, and what permuted a part of the hydrogen atom with a hydroxyl group, a halogen radical, an alkyl group, a carboxyl group, a sulfhydryl group, the amino group, a sulfonic group, etc. can be used for them. As the permutation type concerned of a sulfonic acid, toluenesulfonic acid, a xylene sulfonic acid, p-phenolsulfonic acid, a cresol sulfonic acid, a sulfosalicylic acid, a nitrobenzene sulfonic acid, sulfobenzonic acid, a sulfo phthalic acid, a diphenylamine-4-sulfonic acid, etc. are mentioned, for example.

[0026] As an example of the above-mentioned carboxylic acid, an acetic acid, a propionic acid, butanoic acid, a citric acid, a tartaric acid, a gluconic acid, a sulfo succinic acid, a lactic acid, oxalic acid, a malonic acid, thioglycolic acid, a salicylic acid, a malic acid, etc. are mentioned.

[0027] The parent metal by the side of acceptance plated with a lead free-lancer's tin alloy says iron, nickel, -42% nickel alloy of iron, zinc, aluminum including the copper and the copper alloy which form the circuit pattern of for example, a TAB method, etc. Moreover, as mentioned above, even if the acceptance side concerned gives catalysts, such as palladium, to nonmetal sides, such as plastics and ceramics, it does not interfere.

[0028] what configures the above-mentioned complexing agent in the parent metals concerned, such as copper and a copper alloy, and forms complex ion - it is - the chelating agent of following (1) - (3) etc. - single - business or using together are desirable.

(1) As thiourea and a derivative of the derivative thiourea, 1, 3-dimethyl thiourea, trimethyl thiourea, diethyl thiourea (for example, 1, 3-diethyl-2-thiourea), N, and N'-diisopropyl thiourea, allylthiourea, acetyl thiourea, ethylenethiourea, 1, 3-diphenyl thiourea, a thiourea dioxide, thiosemicarbazide, etc. are mentioned.

(2) Ethylenediaminetetraacetic acid (EDTA), a disodium ethylenediaminetetraacetate salt (EDTA and 2Na), the hydroxyethyl ethylenediamine triacetic acid (HEDTA), a diethylenetriamine pentaacetic acid

(DTPA), triethylenetetramine 6 acetic acid (TTHA), an ethylenediamine tetra-propionic acid, an ethylenediamine tetramethylen phosphoric acid, a diethylenetriamine pentamethylene phosphoric acid, etc.

(3) Nitritotriacetic acid (NTA), iminodiacetate (IDA), imino dipropionic acid (IDP), amino trimethylene phosphoric-acid, and amino trimethylene phosphoric-acid 5 sodium salt, benzylamine, 2-naphthylamine, an isobutyl amine, an isoamyl amine, methylene diamine, ethylenediamine, a tetramethylenediamine, pentaethylene diamine, a hexamethylenediamine, diethylenetriamine, tetraethylenepentamine, pentaethylenhexamine, hexa ethylene HEPUTAMIN, a cinnamyl amine, p-methoxy cinnamyl amine, etc. Generally the addition of the above-mentioned complexing agent is 5 - 200 g/L preferably 0.1 to 300 g/L.

[0029] The above-mentioned reducing agent means the additive of a wide sense also including applications, such as antioxidizing (for example, antioxidizing of stannous salt) of a bath, although added for applications, such as reduction of said metal salt or adjustment of the deposit rate of a bath. therefore, as an example of a reducing agent, phosphorus compounds, a boron compound, a titanium compound, a hydrazine derivative, or polyhydric phenols mention -- having -- the compound concerned -- single -- business -- or it can use together. As the phosphorus compounds concerned, salts, such as hypophosphorous acid, phosphorous acid and these ammonium, a lithium, sodium, a potassium, and calcium, etc. are mentioned. As the boron compound concerned, amine boranes, such as dimethylamine borane, diethylamine borane, trimethylamine borane, isopropylamine borane, and morpholine borane, or a sodium borohydride, a boron hydride potassium, etc. are mentioned. as the titanium compound concerned -- 3 titanium-trichloride and titanium fluoride and sulfuric-acid titanium -- titanium etc. is mentioned 3 bromination 3 titanium iodide. A hydrazine hydrate, methylhydrazine, phenylhydrazine, a semicarbazide, etc. are mentioned as the hydrazine derivative concerned. A hydroquinone, a catechol, resorcinol, pyrogallol, etc. are mentioned as the polyhydric phenols concerned. Generally the addition of the above-mentioned reducing agent is 5 - 150 g/L preferably 0.1 to 200 g/L.

[0030] it adds in order for the above-mentioned surfactant to improve the compactness of a plating coat, adhesion, smooth nature, etc. -- having -- the Nonion system surfactant, an amphoteric surface active agent, a cation system surfactant, and an anion system surfactant -- single -- business -- or although it can use together, the Nonion system or an amphoteric surface active agent is desirable especially. Generally the addition of the above-mentioned surfactant is 1 - 20 g/l preferably 0.01 to 50 g/l)

[0031] As the above-mentioned Nonion system surfactant, nonyl phenol poly-alkoxylate, alpha-(or beta-) naphthol poly alkoxylate, dibutyl-beta-naphthol poly alkoxylate, ether mold Nonion system surfactants, such as styrene-ized phenol poly alkoxylate, cumyl phenol poly alkoxylate, and bisphenol A poly alkoxylate, -- or Amine mold Nonion system surfactants, such as lauryl amine poly alkoxylate, octyl amine poly alkoxylate, hexynil amine poly alkoxylate, and linoleyl amine poly alkoxylate, etc. are mentioned.

[0032] As the above-mentioned amphoteric surface active agent, a 2-undecyl-1-carboxymethyl-1-hydroxyethyl imidazolium betaine, N-stearyl-N, and N-dimethyl-N-carboxymethyl betaine, a lauryldimethyl amine oxide, etc. are mentioned.

[0033] As the above-mentioned cation system surface active agent, it expresses with the form of a salt and a lauryl trimethylammonium salt, lauryldimethyl ammonium betaine, lauryl pyridinium salt, an oleyl imidazolium salt, stearyl amine acetate, etc. are mentioned.

[0034] As the above-mentioned anion system surface active agent, alkylbenzene sulfonates, such as polyoxyalkylene alkylphenyl ethereal sulfate salts, such as polyoxyalkylene alkyl ether sulfate, such as alkyl sulfate, such as sodium lauryl sulfate, and polyoxyethylene (EO12) nonyl ethereal sulfate sodium and polyoxyethylene (EO20) octyl phenyl ether potassium sulfate, and lauryl benzenesulfonic acid ammonium salt, etc. are mentioned.

[0035] As conditions for the above-mentioned electroless deposition bath, although bath temperature is 45-90 degrees C, from the standpoint which gathers a deposit rate, 50-70 degrees C is desirable. In addition, to the plating bath concerned, various additives, such as for example, pH regulator, a buffer, a brightener, a semigloss agent, and a lubricating agent, are mixable if needed in addition to an above-

mentioned compound.

[0036] As for the electronic parts of this invention 5, the tape carrier package of TAB, a resistor, a capacitor, a connector, an inductor, a semi-conductor printed circuit board, etc. are mentioned. For example, this invention 6 is what applied the non-electrolyzed tin alloy plating bath of the lead free-lancer of this inventions 1-4 to TAB, and is the tape carrier package of TAB which formed the tin alloy coat in the inner lead etc. However, in this invention 5, the plating bath of the non-electrolytic bath of both the above-mentioned permutation mold and an autocatalysis mold being included which forms a lead free-lancer's tin alloy coat in electronic parts is natural.

[0037]

[Function] The non-electrolyzed tin alloy plating bath of the lead free-lancer of this invention 1 contains the non-electrolytic bath of a permutation mold and an autocatalysis mold as mentioned above. If the tin-indium alloy plating bath which makes copper a plated field is mentioned as the example of a non-electrolytic bath and there explains the superordinate-concept-operation, according to an operation of the complexing agent which mainly exists during a bath, the inversion of electrode potential arises between the copper of a parent metal, and tin and an indium, tin and an indium are returned to a metal from a metal ion, and a tin-indium alloy coat deposits on the surface of copper. Since an electron is theoretically supplied to the metal ion of tin and an indium from the copper of a parent metal with the permuted type non-electrolytic bath of this invention 2 at this time, during a bath, metal copper serves as a copper ion and is eluted. On the other hand, in an autocatalysis type non-electrolytic bath, theoretically, an electron is supplied from the reducing agent which exists during a bath, it is returned to a metal, and the metal ion of tin and an indium deposits a tin-indium alloy coat. Since the copper of a parent metal itself only serves as a catalyst of a reduction plating reaction in that case, it is not eluted during a bath.

[0038]

[Effect of the Invention]

This invention 1 or 7 (1) A predetermined non-electrolyzed tin alloy plating bath to tin, Since a lead free-lancer's tin alloy coat generated between the specific metals chosen from a bismuth, an indium, antimony, zinc, cobalt, nickel, silver, and copper is obtained While lead poisonous on the body is eliminated from the plating bath and can control the bad influence to health, there is also little risk of environmental pollution and its added value is also high along with the request of a time in respect of safety or prevention of pollution.

[0039] (2) Since the presentation in the deposit coat of the specific metal concerned is 3 % of the weight or more while the electroless deposition coat of this invention is a tin alloy coat generated between tin and specific metals, such as a bismuth, an indium, antimony, and silver, even if it compares the bonding strength of a coat, and corrosion resistance with the non-electrolyzed tin coat used as criteria, they hold high practical use level, and the deposit rate of a bath of coat physical properties is also quick, and the **** effectiveness is large [physical properties].

[0040] That is, as shown in the below-mentioned example of a trial (refer to drawing 1), even if the presentation ratio of the specific metal of this invention compared the tin alloy coat of this invention with the tin coat in 3.3 - 61.7% of the weight of the range, having excelled in a deposit rate, bonding strength, and a corrosion resistance field, or having been equal was admitted. The tin alloy plating coat which stopped the presentation ratio of the above-mentioned specific metal low especially excelled the tin coat in bonding strength or a corrosion resistance field further in many cases.

[0041] Moreover, the non-electrolyzed tin alloy plating bath of this invention had the deposit rate quicker than the non-electrolyzed tin bath, and this inclination was especially remarkable in each tin alloy bath of tin-bismuth, tin-indium, or tin-silver. For this reason, while it becomes easy to carry out plating processing at temperature lower than 80 degrees C and productivity improves, as shown in this invention 5 or 6, every time the tin alloy plating bath of this invention can fully respond also to high-density-assembly articles, such as a TAB method, and lengthens various kinds of electronic parts at first, it can improve the dependability of the products (liquid crystal etc.) using TAB, and the yield of production in a list good.

[0042] (2) Like this invention 3, if additional mixing of the reducing agent is carried out at a lead free-lancer's electroless deposition bath, as mentioned above, the deposit rate of a tin alloy coat is accelerated further, and the **** effectiveness can be promoted further.

[0043] (3) Like this invention 4, to a lead free-lancer's electroless deposition bath, if additional mixing of various kinds of surfactants is carried out, the crystal grain child appearance of a plating coat, smooth nature, adhesion, or compactness is further improvable.

[0044]

[Example] Hereafter, while describing the example of a lead free-lancer's permutation mold radio solution tin alloy plating bath one by one, the corrosion resistance example of a trial is indicated in the deposit rate of the tin alloy coat at the time of plating with each nothing electrolytic bath, and the bonding strength list of the obtained tin alloy plating coat. In addition, as for this invention, it is needless to say that it is not restrained by the following example and many can be changed within the limits of the technical thought of this invention.

[0045] In each examples 1-8 shown below, a sequence has a low presentation ratio in the deposit coat of the specific metal which generates tin and an alloy (however, all 3 % of the weight or more setup), and b sequence raises the presentation ratio.

<<example 1a>> The initial make-up of electrolytic bath of the non-electrolyzed tin-bismuth alloy plating bath was carried out by the following presentation.

- The first tin of methansulfonic acid (as Sn2+) : 40g/L - methansulfonic acid bismuth (as Bi3+) : 5g/L - diethylenetriamine pentaacetic acid (DTPA) : 30g/L - methansulfonic acid : 80g/L - 1, 3-dimethyl thiourea : 120 g/L - calcium hypophosphite : 30 g/L - dibutyl-beta-naphthol polyethoxylate (EO15) : 15 g/L This tin-bismuth alloy plating bath is held at 65 degrees C. -NaOH - pH 2 - **** - The test piece of the film carrier of TAB which carried out pattern formation by VLP (a kind of electrolytic copper foil) was immersed for 10 minutes, and electroless deposition was performed. The coat of obtained tin-bismuth alloy plating had the thickness of 1.8 micrometers, and 8.0% of bismuth content (presentation ratio), and a plating appearance, adhesion, and the compactness of a particle were satisfactory level.

[0046] <<example 1b>> The initial make-up of electrolytic bath of the non-electrolyzed tin-bismuth alloy plating bath was carried out by the following presentation.

- The first tin of methansulfonic acid (as Sn2+) : 30 g/L - bismuth oxide (as Bi3+) : 15g/L - 2-butane sulfonic acid : 80g/L - 1, 3-dimethyl thiourea : 120 g/L - calcium hypophosphite : 30 g/L - linoleyl amine polyethoxylate (EO12) -poly propoxy rate (PO3) : The film carrier of TAB was immersed in this tin-bismuth alloy plating bath 12 g/L, and electroless deposition was performed on the same conditions as said example 1a. The coat of obtained tin-bismuth alloy plating had the thickness of 3.2 micrometers, and 38.0% of bismuth content, and a plating appearance, adhesion, and the compactness of a particle were satisfactory level.

[0047] <<example 2a>> The initial make-up of electrolytic bath of the non-electrolyzed tin-indium alloy plating bath was carried out by the following presentation.

- The first tin of ethane sulfonic acid (as Sn2+) : 30 g/L - indium oxide (as In3+) : 20g/L - ethane sulfonic acid : 70 g/L - allylthiourea : 150 g/L - hydrazine hydrochloride : 65g/L - lauryldimethyl amine oxide : 15g/L - the film carrier of TAB was immersed in this tin-indium alloy plating bath, and electroless deposition was performed on the same conditions as said example 1a. The coat of the obtained tin-indium alloy plating had the thickness of 1.0 micrometers, and 3.3% of indium content, and a plating appearance, adhesion, and the compactness of a particle were satisfactory level.

[0048] <<example 2b>> The initial make-up of electrolytic bath of the non-electrolyzed tin-indium alloy plating bath was carried out by the following presentation.

- A 1-hydroxy propane - The first tin of 2-sulfonic acid (as Sn2+) : 15g/L - methansulfonic acid indium (as In3+) : 50g/L - ethane sulfonic acid : 70 g/L - thiourea : 150 g/L - hypophosphorous acid potassium : 65g/L - octylamine polyethoxylate (EO8) : The film carrier of TAB was immersed in this tin-indium alloy plating bath 10 g/L, and electroless deposition was performed on the same conditions as said example 1a. The coat of the obtained tin-indium alloy plating had the thickness of 1.5 micrometers, and 32.6% of indium content, and a plating appearance, adhesion, and the compactness of a particle were

satisfactory level.

[0049] <<example 3a>> The initial make-up of electrolytic bath of the non-electrolyzed tin-regulus metal plating bath was carried out by the following presentation.

- The first tin of methansulfonic acid (as Sn^{2+}) : 20 g/L - tartaric-acid antimony (as Sb^{3+}) : 20g/L - 2-naphthalene sulfonic acid : 55 g/L - tartaric acid : 50 g/L - diphenyl thiourea : 140 g/L - hypophosphorous acid : 45 g/L - polyoxyethylene (EO12) nonyl ether - sodium sulfate : The film carrier of TAB was immersed in this tin-regulus metal plating bath 10 g/L, and electroless deposition was performed on the same conditions as said example 1a. The coat of obtained tin-regulus metal plating had the thickness of 0.65 micrometers, and 4.5% of antimony content, and a plating appearance, adhesion, and the compactness of a particle were satisfactory level.

[0050] <<example 3b>> The initial make-up of electrolytic bath of the non-electrolyzed tin-regulus metal plating bath was carried out by the following presentation.

- The first tin of p-phenolsulfonic acid (as Sn^{2+}) : 8 g/L - tartaric-acid antimony (as Sb^{3+}) : 50 g/L - xylene sulfonic acid : 80 g/L - acetic acid : 15g/L - 1, 3-diphenyl thiourea : 140 g/L - hypophosphorous acid : 45g/L - t-butanol polyethoxylate (EO10) : The film carrier of TAB was immersed in this tin-regulus metal plating bath 10 g/L, and electroless deposition was performed on the same conditions as said example 1a. The coat of obtained tin-regulus metal plating had the thickness of 0.88 micrometers, and 41.2% of antimony content, and a plating appearance, adhesion, and the compactness of a particle were satisfactory level.

[0051] <<example 4a>> The initial make-up of electrolytic bath of the non-electrolyzed tin-zinc alloy plating bath was carried out by the following presentation.

- The first tin of methansulfonic acid (as Sn^{2+}) : 30 g/L - methansulfonic acid zinc (as Zn^{2+}) : 40 g/L - citric acid : 120 g/L - thiourea : 180 g/L - dimethylamine borane : 100 g/L - N-dodecyl-N and N-dimethyl -N-carboxymethyl betaine : 20g/L - the film carrier of TAB was immersed in this tin-zinc alloy plating bath, and electroless deposition was performed on the same conditions as said example 1a. The coat of obtained tin-zinc alloy plating had the thickness of 0.8 micrometers, and 5.5% of zinc content, and a plating appearance, adhesion, and the compactness of a particle were satisfactory level.

[0052] <<example 4b>> The initial make-up of electrolytic bath of the non-electrolyzed tin-zinc alloy plating bath was carried out by the following presentation.

- 2-hydroxy butane - The first tin of 1-sulfonic acid (as Sn^{2+}) : 20 g/L - zinc sulfate (as Zn^{2+}) : 53g/L - nitrobenzene sulfonic acid : 110 g/L - thiourea : 200 g/L - hypophosphorous acid ammonium : 100 g/L - dibenzyl phenol polyethoxylate (EO12) : The film carrier of TAB was immersed in this tin-zinc alloy plating bath 24 g/L, and electroless deposition was performed on the same conditions as said example 1a. The coat of obtained tin-zinc alloy plating had the thickness of 0.72 micrometers, and 33.3% of zinc content, and a plating appearance, adhesion, and the compactness of a particle were satisfactory level.

[0053] <<example 5a>> The initial make-up of electrolytic bath of the non-electrolyzed tin-nickel alloy plating bath was carried out by the following presentation.

- A 2-hydroxy propane - The first tin of 1-sulfonic acid (as Sn^{2+}) : 35 g/L - nickel sulfate (as nickel $^{2+}$) : 6.5 g/L - malic acid : 50g/L - acetyl thiourea : 175 g/L - hypophosphorous acid ammonium : 80 g/L - 1 and 1-screw (4-hydroxyphenyl)

- Ethane polyethoxylate (EO10) : The film carrier of TAB was immersed in this tin-nickel alloy plating bath 10 g/L, and electroless deposition was performed on the same conditions as said example 1a. The coat of obtained tin-nickel alloy plating had the thickness of 0.85 micrometers, and 4.0% of nickel content, and a plating appearance, adhesion, and the compactness of a particle were satisfactory level.

[0054] <<example 5b>> The initial make-up of electrolytic bath of the non-electrolyzed tin-nickel alloy plating bath was carried out by the following presentation.

- A 2-hydroxy propane - The first tin of 1-sulfonic acid (as Sn^{2+}) : 15 g/L - nickel sulfate (as nickel $^{2+}$) : 25 g/L - butanoic acid : 55 g/L - thiourea dioxide : 175 g/L - hypophosphorous acid : 80 g/L - t-butanol polyethoxylate (EO10) : The film carrier of TAB was immersed in this tin-nickel alloy plating bath 14 g/L, and electroless deposition was performed on the same conditions as said example 1a. The coat of obtained tin-nickel alloy plating had the thickness of 0.55 micrometers, and 56.0% of nickel content, and

a plating appearance, adhesion, and the compactness of a particle were satisfactory level.

[0055] <<example 6a>> The initial make-up of electrolytic bath of the non-electrolyzed tin-cobalt alloy plating bath was carried out by the following presentation.

- The first tin of 2-propane sulfonic acid (as Sn^{2+}): 10 g/L - cobalt sulfate (as Co^{2+}): 5 g/L - p-phenolsulfonic acid: 50 g/L - tartaric acid: 10g/L - diethyl thiourea: 110 g/L - hypophosphorous acid: 15g/L - alpha-naphthol polyethoxylate (EO15): The film carrier of TAB was immersed in this tin-cobalt alloy plating bath 8 g/L, and electroless deposition was performed on the same conditions as said example 1a. The coat of obtained tin-cobalt alloy plating had the thickness of 0.65 micrometers, and 3.6% of cobalt content, and a plating appearance, adhesion, and the compactness of a particle were satisfactory level.

[0056] <<example 6b>> The initial make-up of electrolytic bath of the non-electrolyzed tin-cobalt alloy plating bath was carried out by the following presentation.

- The first tin of 2-propane sulfonic acid (as Sn^{2+}): 8 g/L - cobalt sulfate (as Co^{2+}): 25 g/L - sulfuric acid: 50 g/L - citric acid: 18 g/L - thiourea: 110 g/L - sodium borohydride: 15 g/L - lauryldimethyl ammonium betaine: 3 g/L - NaOH - pH 7 - **** - the film carrier of TAB was immersed in this tin-cobalt alloy plating bath, and electroless deposition was performed on the same conditions as said example 1a. The coat of obtained tin-cobalt alloy plating had the thickness of 0.53 micrometers, and 35.1% of cobalt content, and a plating appearance, adhesion, and the compactness of a particle were satisfactory level.

[0057] <<example 7a>> The initial make-up of electrolytic bath of the non-electrolyzed tin-copper alloy plating bath was carried out by the following presentation (cuprous salt is used).

- The first tin of toluenesulfonic acid (as Sn^{2+}): 30g/L - cuprous oxide (as Cu^{+}): 10 g/L - propionic acid: 80g/L - thiosemicarbazide: 100 g/L - calcium hypophosphite: 10 g/L - stearyl amine acetate: The film carrier of TAB was immersed in this tin-copper alloy plating bath 4 g/L, and electroless deposition was performed on the same conditions as said example 1a. The coat of obtained tin-copper alloy plating had the thickness of 0.87 micrometers, and 7.5% of copper content, and a plating appearance, adhesion, and the compactness of a particle were satisfactory level.

[0058] <<example 7b>> The initial make-up of electrolytic bath of the non-electrolyzed tin-copper alloy plating bath was carried out by the following presentation (cupric salt is used).

- The first tin of a cresol sulfonic acid (as Sn^{2+}): 16 g/L - p-phenolsulfonic acid copper (as Cu^{2+}): 60g/L - ethane sulfonic acid: 120g/L - ethylenethiourea: 100 g/L - sodium hypophosphite: 10 g/L - hexynil amine polyethoxylate (EO10): The film carrier of TAB was immersed in this tin-copper alloy plating bath 4 g/L, and electroless deposition was performed on the same conditions as said example 1a. The coat of obtained tin-copper alloy plating had the thickness of 0.7 micrometers, and 37.8% of copper content, and a plating appearance, adhesion, and the compactness of a particle were satisfactory level.

[0059] <<example 8a>> The initial make-up of electrolytic bath of the non-electrolyzed tin-silver alloy plating bath was carried out by the following presentation.

- The first tin of p-phenolsulfonic acid (as Sn^{2+}): 32 g/L - silver nitrate (as Ag^{+}): 5 g/L - pyrophosphoric acid: 100 g/L - potassium iodide: 120 g/L - thiourea: 120 g/L - hypophosphorous acid ammonium: 55 g/L - octylamine polyethoxylate (EO8): 18 g/L - KOH - pH8 - **** - the film carrier of TAB was immersed in this tin-silver alloy plating bath, and electroless deposition was performed on the same conditions as said example 1a. The coat of obtained tin-silver alloy plating had the thickness of 1.2 micrometers, and 9.8% of silver content, and a plating appearance, adhesion, and the compactness of a particle were satisfactory level.

[0060] <<example 8b>> The initial make-up of electrolytic bath of the non-electrolyzed tin-silver alloy plating bath was carried out by the following presentation.

- 2-hydroxy ethane - The first tin of 1-sulfonic acid (as Sn^{2+}): 55 g/L - silver nitrate (as Ag^{+}): 15g/L - 1-butane sulfonic acid: 100 g/L - potassium iodide: 135g/L - trimethyl thiourea: 120 g/L - hypophosphorous acid ammonium: 35 g/L - styrene-ized phenol polyethoxylate (EO18): 18 g/L - KOH - pH 9 - **** - the film carrier of TAB was immersed in this tin-silver alloy plating bath, and electroless deposition was performed on the same conditions as said example 1a. The coat of obtained

tin-silver alloy plating had the thickness of 1.4 micrometers, and 61.7% of silver content, and a plating appearance, adhesion, and the compactness of a particle were satisfactory level.

[0061] Example of <<comparison>> The initial make-up of electrolytic bath of the non-electrolyzed tinning bath was carried out by the following presentation.

- The first tin of methansulfonic acid (as Sn^{2+}) : 15g/L - methansulfonic acid : 50 g/L - thiourea : 100 g/L - sodium hypophosphite : 25 g/L - dibutyl-beta-naphthol polyethoxylate (EO15) : 15 g/L, this tinning bath was held at 65 degrees C, the test piece of the film carrier of TAB which carried out pattern formation by VLP was made immersed for 10 minutes, and electroless deposition was performed. The coat of obtained tinning had 0.48-micrometer thickness.

[0062] Example of trial>> of <<deposit rate Each radio solution tin alloy plating bath of above-mentioned example 1 a-b - 8 a-b was used, and although the thickness at the time of plating with 65 degrees C and the conditions for 10 minutes on the tape carrier package of TAB was as having mentioned above for every example, it evaluated the **** capacity (speed of a deposit rate) of each radio solution tin alloy plating bath by thickness of these 10 minutes after. Three left-leaning columns of drawing 1 R> 1 showed the content of the specific metal which generates the class, the tin, and the alloy of a plating coat, and thickness, respectively, and showed evaluation of **** capacity from the left to eye four columns. However, the valuation basis of **** capacity is as follows, and the quality judged the non-electrolyzed tinning bath as an example of reference.

valuation-basis O: of a deposit rate -- thickness -- more than 0.5 micrometerx: -- thickness -- less than 0.5 micrometers [0063] <<bonding strength and corrosion resistance example of trial>> Bonding of the tape carrier package of each TAB which performed electroless deposition using the tin alloy bath of the above-mentioned example was carried out on the predetermined copper plate, and bonding strength was investigated. That is, the bonding machine (TCW[by the avionics company]-115A) was used, and bonding of the inner lead of each TAB was carried out to the copper plate which performed 0.5-micrometer gold plate under 50g of loads/, a unit inner lead, the temperature of 450 degrees C, and the conditions for time amount 5 seconds. And it pulled until it fractured the end of the inner lead after bonding in the direction of a right angle to the above-mentioned copper plate, and the simple trial of the peeling reinforcement (peel strength) of a lead was performed by investigating the shearing mode.

[0064] Moreover, the corrosion resistance test was performed in the following way. after [namely,] TAB of the above-mentioned example is immersed in 1% hypochlorous-acid water solution warmed at 60 degrees C for 24 hours, respectively -- an appearance -- observing -- rust, a spot, the existence of a stain, or an overall color -- strange ** was investigated.

[0065] Eye two columns shows respectively the result of corrosion resistance [column / of this drawing / rightmost] for the result of bonding strength from the right of drawing 1 . In addition, bonding strength and each corrosion resistance valuation basis are as follows, and the quality was judged on the basis of the non-electrolyzed tinning coat of the example of a comparison.

(1) Valuation-basis [of bonding strength] O : excel the tinning coat of the example of a comparison.

O : equivalent to the tinning coat of the example of a comparison.

** : It is inferior to the tinning coat of the example of a comparison.

(2) Corrosion resistance valuation-basis O : excel the tinning coat of the example of a comparison.

O : equivalent to the tinning coat of the example of a comparison.

** : It is inferior to the tinning coat of the example of a comparison.

[0066] Evaluation>> of the <<above-mentioned test result By the tin coat of the example of a comparison, the **** capacity (speed of a deposit rate; it measures by the thickness of 10 minutes after) of a lead free-lancer's electroless deposition bath exceeded the numeric value of a tin coat in the tin alloy coat of example 1 a-b - 8 a-b, specifically showed 0.53 micrometers or more to having been 0.48 micrometers, and was evaluation of O altogether. However, the thickness of a tin alloy coat and the relation between tin and the presentation ratio in the deposit coat concerned of the specific metal which generates an alloy (content) Although thickness also increased when it changed with the classes of tin alloy coat, for example, the content of the above-mentioned specific metal increased in the various alloy coats of a tin-bismuth, a tin-indium, tin-antimony, and tin-silver On the contrary, in the various alloy

coats of tin-zinc, tin-nickel, tin-cobalt, and tin-copper, when the content of the above-mentioned specific metal increased, thickness decreased. Moreover, especially the thickness of the tin-bismuth alloy coat of example 1b showed 3.20 micrometers which is the maximum of all the examples. Furthermore, the tin-indium alloy coat of example 2b and the tin-silver alloy coat of example 8b reached about 3 times as much thickness as the tin coat of the example of a comparison.

[0067] About bonding strength, the tin alloy coat of the lead free-lancer of each example 1 a-b - 8 a-b is superior to the tin coat of the example of a comparison, or is equivalent in many cases, evaluation is O-O in general, and evaluation of ** remained in three examples. Moreover, when the tin alloy coats of the same class were compared, the examples 1-8 of a sequence with the high content of tin excelled the examples 1-8 of b sequence with the low content of tin in evaluation of bonding strength. In this case -- it should observe -- the examples 1-8 of a sequence with the low content of the above-mentioned specific metal are the points that bonding strength won the tin coat by any tin alloy coat of a class.

[0068] It excelled [whether the tin alloy coat of each example is equivalent to the tin coat of the example of a comparison, and] about corrosion resistance, and all evaluations were O-O. Especially as for the tin-nickel alloy coat of example 5a, the tin-cobalt alloy coat of example 6a, and the tin-copper alloy coat of example 7a, corrosion resistance won the tin coat of the example of a comparison.

[0069] As mentioned above, since the level which the non-electrolyzed tin alloy-plating bath of this example whose presentation ratio in the deposit coat of the above-mentioned specific metal which generates tin and an alloy it is a lead free-lancer and is 3 % of the weight or more has a quick deposit rate compared with a non-electrolyzed tin bath, the acquired bonding strength of a plating coat and the corrosion resistance also excel compared with a non-electrolyzed tin coat in being able to improve the productivity of plating, or is equal is securable, very high practicality was accepted.

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